SUPPLEMENTARY MATERIAL

Exploring intra- and intermolecular interactions in selected *N*-oxides - the role of hydrogen bonds

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IX. **MICROSOLVATION MODELS OF THE COMPOUND 1.**

Sets of coordinates obtained at the B3LYP/6-311++G(d,p) level of theory.

Sets of coordinates obtained at the ωB97XD/6-311++G(d,p) level of theory.

X. **Figure S4.** Microsolvation models of the compound **2** obtained at the ωB97XD/6-311++G(d,p) level of theory.

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XII. **Table S7.** Metric parameters of the intra- and intermolecular hydrogen bonds obtained as a result of microsolvation of the compound **2** (ωB97XD/6-311++G(d,p) level of theory). The interatomic distances are given in Å while valence angle is given in [°].

XIII. **MICROSOLVATION MODELS OF THE COMPOUND 2.**

Sets of coordinates obtained at the B3LYP/6-311++G(d,p) level of theory.

Sets of coordinates obtained at the ωB97XD/6-311++G(d,p) level of theory.

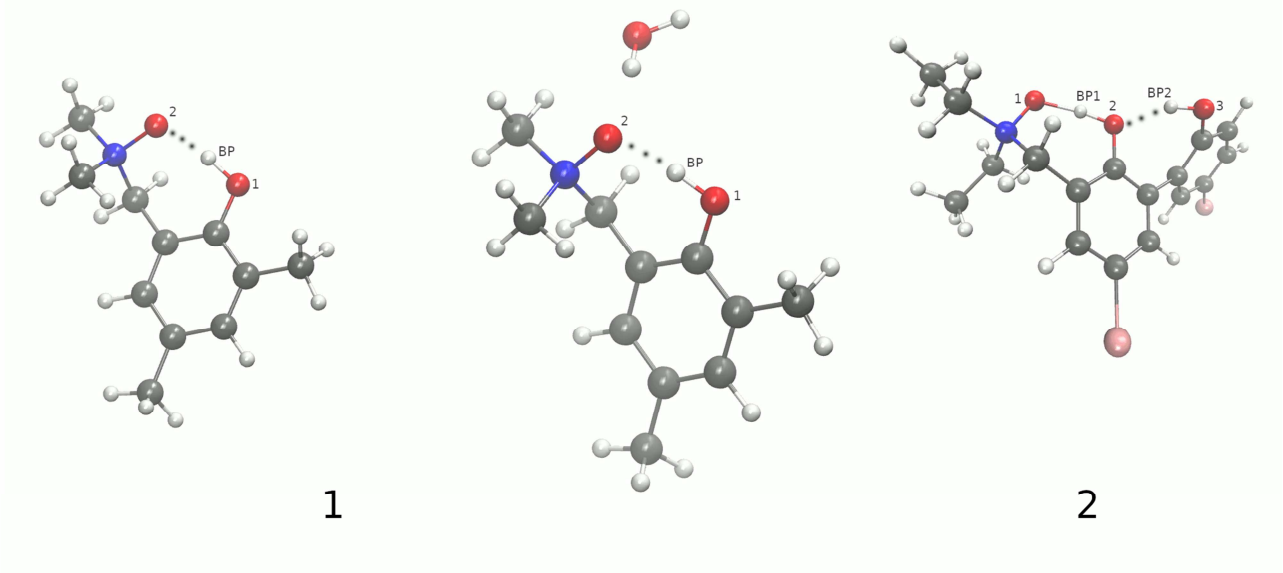

Figure S1. The structures of the investigated *N*-oxides with atoms numbering scheme. BP indicates the bridged protons while the dotted line – the presence of intramolecular hydrogen bond. Coloring code: oxygen – red, nitrogen – blue, carbon – grey, hydrogen – white and bromine – pink.

Table S1. Interatomic distances of atoms involved in the intramolecular hydrogen bonds in **compound 1 (isolated molecule)**. Comparison between experimental (X-ray) [1] and computed at the DFT level of theory data. The 6-311++G(d,p) basis set was applied during the simulations. The data was obtained in the gas phase and with solvent reaction field using IEF-PCM model and water as a solvent. The interatomic distances are given in Å while valence angle is given in [°].

Metric parameters	**Exp. X-ray [1]**	**Gas phase**				**Polarizable Continuum Model**			
		B3LYP	**CAM-B3LYP**	**M05-2X**	**ωB97XD**	**B3LYP**	**CAM-B3LYP**	**M05-2X**	**ωB97XD**
O1...O2	2.541	2.5564	2.5427	2.5161	2.5608	2.5347	2.5214	2.4854	2.5407
O1-HBP	1.135	1.0171	1.0147	1.0246	1.0082	1.0239	1.0213	1.0386	1.0132
HBP...O2	1.458	1.5514	1.5421	1.5049	1.5664	1.5193	1.5101	1.4557	1.5374
<O1HBPO2	156.85	168.63	167.71	167.92	167.89	170.51	169.64	170.15	169.71

*the experimental data was recorded for the monohydrated form of the compound **1**. Therefore the X-ray values serve only as references for our quantum-mechanical simulations for the isolated molecule.

the Cambridge Crystallographic Data Center (CCDC) identifier for the **compound 1 is: SEHBEM with the database number: 593412.

Table S2. Interatomic distances of atoms involved in the intramolecular hydrogen bonds in **compound 1 (monohydrate)**. Comparison between experimental (X-ray) [1] and computed at DFT level of theory data. The 6-311++G(d,p) basis set was applied during the simulations. The data was obtained in the gas phase and with solvent reaction field using IEF-PCM model and water as a solvent. The interatomic distances are given in Å while valence angle is given in [°].

Metric parameters	**Exp. X-ray [1]**	**Gas phase**				**Polarizable Continuum Model**			
		B3LYP	**CAM-B3LYP**	**M05-2X**	**ωB97XD**	**B3LYP**	**CAM-B3LYP**	**M05-2X**	**ωB97XD**
Intramolecular hydrogen bond									
O1...O2	2.541	2.5882	2.5748	2.5541	2.5905	2.5694	2.5553	2.5324	2.5787
O1-HBP	1.135	1.0073	1.0047	1.0099	0.9991	1.0097	1.0068	1.0135	1.0013
HBP...O2	1.458	1.5894	1.5794	1.5533	1.6013	1.5717	1.5625	1.5336	1.5874
<O1HBPO2	156.85	170.44	170.03	170.14	169.73	168.68	167.73	167.41	169.67
Intermolecular hydrogen bond									
O2...O	2.718	2.7777	2.7348	2.7614	2.7498	2.7275	2.6946	2.7189	2.7307
O-H	0.964	0.9816	0.9815	0.9755	0.9781	0.9866	0.9866	0.9808	0.9814
O2...H	1.755	1.8227	1.7902	1.8317	1.8084	1.7427	1.7085	1.7403	1.7500
O2HO	177.46	163.44	160.42	158.22	160.47	175.64	177.66	175.10	177.32

the Cambridge Crystallographic Data Center (CCDC) identifier for the **compound 1 is: SEHBEM with the database number: 593412.

Table S3. Interatomic distances of atoms involved in the intramolecular hydrogen bonds in **compound 2**. Comparison between experimental (X-ray) [2] and computed at DFT level of theory data. The 6-311++G(d,p) basis set was applied during the simulations. The data was obtained in the gas phase and with solvent reaction field using IEF-PCM model and water as a solvent. The interatomic distances are given in Å while valence angle is given in [°].

Metric parameters	**Exp. X-ray [2]**	**Gas phase**				**Polarizable Continuum Model**			
		B3LYP	**CAM-B3LYP**	**M05-2X**	**ωB97XD**	**B3LYP**	**CAM-B3LYP**	**M05-2X**	**ωB97XD**
O2...O1	2.419	2.4559	2.4459	2.4215	2.4636	2.4695*	2.4466*	2.4291*	2.4729*
O2-HBP1	1.215	1.0663	1.0626	1.0946	1.0479	1.4152*	1.3865*	1.3495*	1.4344*
HBP1...O1	1.205	1.3952	1.3902	1.3318	1.4228	1.0565*	1.0627*	1.0820*	1.0425*
<O1HBP1O2	178.71	172.28	171.36	172.65	171.21	175.15*	174.69*	174.83*	173.36*
O2...O3	2.529	2.6363	2.6176	2.6309	2.6436	2.5444	2.5306	2.5294	2.5509
O3-HBP2	1.284	0.9791	0.9779	0.9755	0.9734	1.0025	1.0008	1.0005	0.9953
HBP2...O2	1.245	1.7195	1.7033	1.7201	1.7380	1.5741	1.5637	1.5651	1.5907
<O3HBP2O2	179.60	154.34	154.01	153.81	153.22	161.39	160.85	160.23	160.59

*indicates that the bridged proton moved to the acceptor side

the Cambridge Crystallographic Data Center (CCDC) identifier for the **compound 2 is: WUKMOE with the database number: 178615.

Table S4. The energy of conformers of **1** and **2** computed at the B3LYP/6-311++G(d,p) and ωB97XD/6-311++G(d,p) levels of theory. The values of energy are given in kcal/mol.

Level of theory	B3LYP/6-311++G(d,p)		ωB97XD/6-311++G(d,p)	
	Gas phase	PCM	Gas phase	PCM
Compound 1*				
A	-398299.043	-398309.856	-398168,700	-398179,869
B	---	-398297.785	---	-398167,881
Compound 1 (monohydrate)*				
A	-446286.714	-446299.528	-446142.652	-446154.563
B	-446273.171	-446289.713	---	-446145.995
Compound 2				
A	-3820383.622	-3820396.998 (proton transfer to the N→O moiety)	-3820229.650	-3820243.133 (proton transfer to the N→O moiety)
B	-3820377.413	-3820391.784	-3820223.445	-3820238.145
C	-3820362.620	-3820380.499	-3820208.319	-3820226.876

*for the isolated molecule of **1** there was not found an open form in the gas phase for both functionals. The same holds for monohydrate form of the computed **1** computed at the ωB97XD/6-311++G(d,p) level of theory in the gas phase.

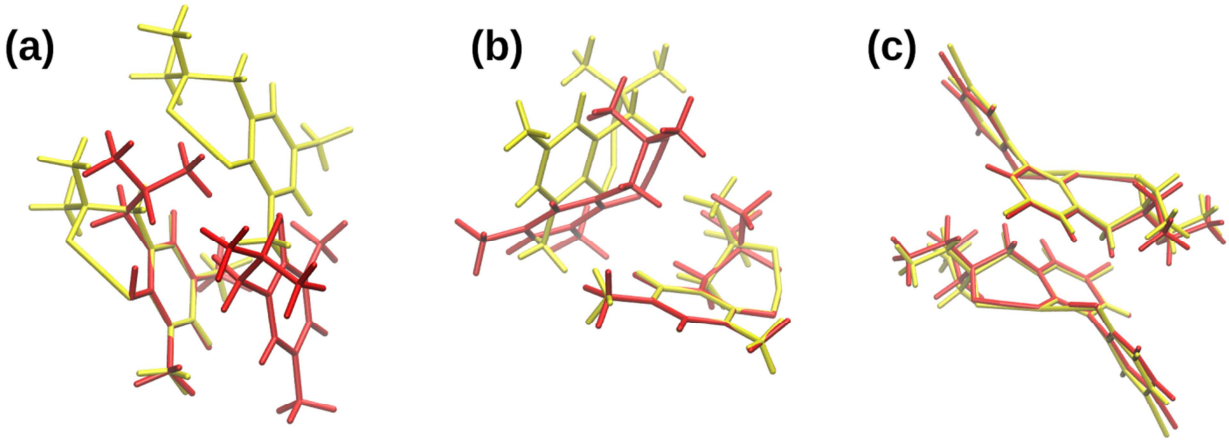

Figure S2. The overlap of the X-ray (yellow) and optimized (red) structures of the dimers used in the SAPT study: (a) dimer 1 of the compound **1**, (b) dimer 2 of the compound **1** and (c) dimer 1 of the compound **2**.

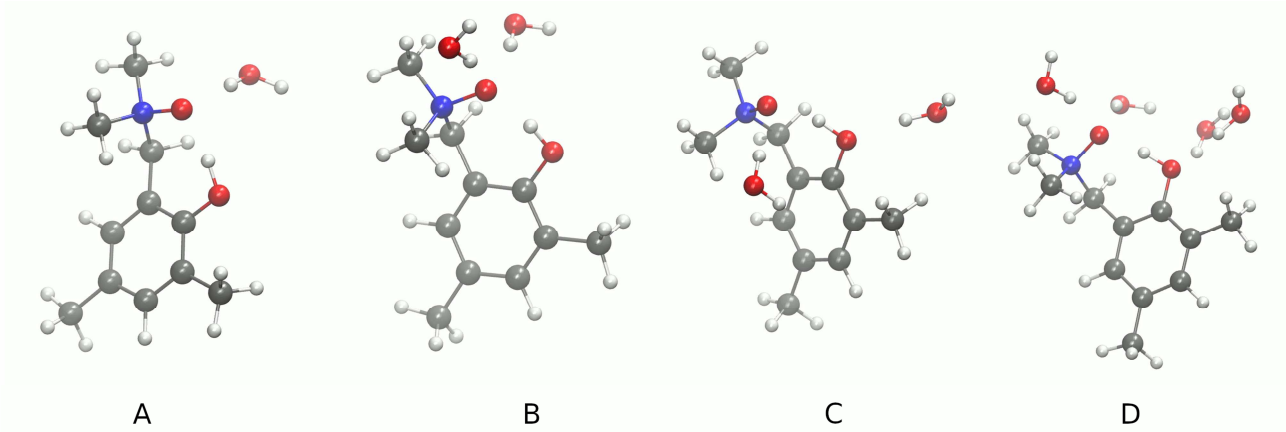

Figure S3. Microsolvation models of the compound **1** obtained at the ωB97XD/6-311++G(d,p) level of theory.

Table S5. Metric parameters of the intra- and intermolecular hydrogen bonds obtained as a result of microsolvation of the compound **1**. The interatomic distances are given in Å while valence angle is given in [°].

Compound 1								
	B3LYP/6-311++G(d,p)				**ωB97XD/6-311++G(d,p)**			
	Model A							
	Intramolecular hydrogen bond (interatomic distances)							
	O1...O2	O1-HBP	HBP...O2	<O1HBPO2	O1...O2	O1-HBP	HBP...O2	<O1HBPO2
	2.5882	1.0073	1.5894	170.44	2.5905	0.9991	1.6013	169.73
	Intermolecular hydrogen bond (interatomic distances)							
	O2...O	O-H	O2...H	<O2HO	O2...O	O-H	O2...H	<O2HO
	2.7777	0.9816	1.8227	163.44	2.7498	0.9781	1.8084	160.47
	Model B							
	Intramolecular hydrogen bond (interatomic distances)							
	O1...O2	O1-HBP	HBP...O2	<O1HBPO2	O1...O2	O1-HBP	HBP...O2	<O1HBPO2
	2.6113	0.9994	1.6300	170.14	2.6089	0.9921	1.6284	168.91
	Intermolecular hydrogen bonds (interatomic distances)							
	O2...O	O-H	O2...H	<O2HO	O2...O	O-H	O2...H	<O2HO
H_2O (1)	2.7629	0.9804	1.8273	158.49	2.7364	0.9768	1.8071	157.78
H_2O (2)	2.8057	0.9787	1.8592	161.83	2.7781	0.9749	1.8370	161.32

Table S5 (Continuation). Metric parameters of the intra- and intermolecular hydrogen bonds obtained as a result of microsolvation of the compound **1**. The interatomic distances are given in Å while valence angle is given in [°].

Compound 1								
	B3LYP/6-311++G(d,p)				**ωB97XD/6-311++G(d,p)**			
	Model C							
	Intramolecular hydrogen bond (interatomic distances)							
	O1...O2	O1-HBP	HBP...O2	<O1HBPO2	O1...O2	O1-HBP	HBP...O2	<O1HBPO2
	2.4734	1.0544	1.4261	171.23	2.5573	1.0040	1.5880	160.73
	Intermolecular hydrogen bonds (interatomic distances)							
	O1...O	O-H	O1...H	<O1HO	O2...O	O-H	O2...H	<O2HO
H_2O	2.7676	0.9814	1.7995	168.26	2.8700	0.9722	1.9088	165.69
	---	---	---	---	O1...O	O-H	O1...H	<O1HO
	---	---	---	---	2.8307	0.9682	1.8668	173.32
	Model D							
	B3LYP/6-311++G(d,p)				**ωB97XD/6-311++G(d,p)**			
	Intramolecular hydrogen bond (interatomic distances)							
	O1...O2	O1-HBP	HBP...O2	<O1HBPO2	O1...O2	O1-HBP	HBP...O2	<O1HBPO2
	2.5448	1.0206	1.5307	171.65	2.5328	1.0143	1.5267	170.58
	Intermolecular hydrogen bonds (interatomic distances)							
	O2...O	O-H	O2...H	<O2HO	O2...O	O-H	O2...H	<O2HO
H_2O (1)	2.7604	0.9805	1.8211	159.37	2.7412	0.9759	1.8114	158.09
H_2O (2)	2.9436	0.9692	2.0813	147.26	2.8951	0.9665	2.0071	151.79
	O1...O	O-H	O1...H	<O1HO	O1...O	O-H	O1...H	<O1HO
H_2O (1)	2.7903	0.9792	1.8128	175.92	2.8290	0.9683	1.9147	156.47
H_2O (2)	---	---	---	---	2.9572	0.9636	2.1026	146.93

MICROSOLVATION MODELS OF THE COMPOUND 1

Sets of coordinates obtained at the B3LYP/6-311++G(d,p) level of theory

Compound 1

Model A - monohydrated form

34

scf done: -711.203686

O	16.387287	1.562442	1.413093
O	17.733176	2.005451	3.578938
N	17.074276	3.065476	4.195723
C	15.250822	2.261370	1.603347
C	15.173909	3.364542	2.474735
C	13.942928	4.019110	2.641267
C	12.799343	3.630304	1.953804
C	12.915976	2.548890	1.068650
C	14.108398	1.860460	0.877235
C	16.393874	3.946061	3.136386
C	18.088478	3.892966	4.930163
C	16.081107	2.509435	5.165402
C	11.481362	4.345423	2.135749
C	14.214358	0.698428	-0.074515
H	16.988827	1.684023	2.211849
H	13.893228	4.872345	3.312839
H	12.040099	2.228349	0.510597
H	16.129216	4.882656	3.630640
H	17.197225	4.137075	2.422521
H	18.780123	4.308463	4.200623
H	18.624291	3.221716	5.597471
H	17.586787	4.682309	5.492355
H	15.387153	1.883622	4.612151
H	16.635964	1.909916	5.883189
H	15.547386	3.322558	5.660925
H	10.704216	3.666917	2.502329
H	11.121892	4.768632	1.192333
H	11.570649	5.164653	2.852804
H	14.946932	0.899420	-0.861781

H	13.250806	0.489050	-0.543232
H	14.557482	-0.202231	0.442293
O	20.008108	3.181740	2.503488
H	19.280948	2.607789	2.828091
H	20.317376	2.780940	1.686637

Model B

37

scf done: -787.676848

O	16.350714	1.517713	1.375271
O	17.696746	1.874759	3.584199
N	17.048042	2.936876	4.227393
C	15.234474	2.252054	1.576499
C	15.187226	3.331235	2.478336
C	13.976874	4.021895	2.649958
C	12.828609	3.691384	1.939988
C	12.918122	2.631932	1.026218
C	14.088936	1.908596	0.828459
C	16.416871	3.855141	3.171052
C	18.071724	3.718585	5.002084
C	16.017746	2.384051	5.164167
C	11.532418	4.442473	2.132428
C	14.165184	0.768665	-0.152614
H	16.942220	1.594388	2.177195
H	13.947796	4.856865	3.344955
H	12.038367	2.356474	0.450648
H	16.174851	4.787608	3.683446
H	17.238220	4.039188	2.476169
H	18.784644	4.133738	4.292893
H	18.569772	3.021465	5.672659
H	17.573317	4.510146	5.563398
H	15.323052	1.785805	4.581679
H	16.535194	1.763914	5.892614
H	15.491811	3.207779	5.649440
H	10.743290	3.787464	2.516027

H	11.171379	4.865526	1.189798
H	11.652395	5.265433	2.840574
H	14.912836	0.963562	-0.927093
H	13.200148	0.605844	-0.636260
H	14.469776	-0.156906	0.343960
H	19.154754	2.577297	2.669204
O	19.796400	3.210696	2.288563
H	20.009951	2.876443	1.412893
H	18.385726	0.797781	4.889764
O	18.610221	0.488161	5.792516
H	19.243214	-0.226806	5.687024

Model C

37

scf done: -787.676234

O	15.635515	0.765330	1.915398
O	16.856615	1.367923	3.980263
N	16.844051	2.753160	4.091964
C	14.684906	1.731577	1.871810
C	14.943293	3.017120	2.380445
C	13.924737	3.979034	2.353743
C	12.668695	3.704521	1.819933
C	12.453945	2.424082	1.293460
C	13.431724	1.432466	1.305502
C	16.333931	3.409002	2.804286
C	18.254453	3.207247	4.323455
C	15.981216	3.121138	5.256169
C	11.572524	4.743873	1.800479
C	13.179895	0.059046	0.740828
H	16.214633	0.952819	2.776393
H	14.132519	4.973640	2.739493
H	11.484349	2.187548	0.863004
H	16.387657	4.487787	2.965317
H	17.077845	3.134982	2.054251
H	18.833815	2.934649	3.443544

H	18.619383	2.675365	5.199201
H	18.278290	4.286961	4.486011
H	14.975722	2.765178	5.047723
H	16.383176	2.609039	6.127302
H	15.985227	4.203265	5.402097
H	10.727532	4.446488	2.430469
H	11.183460	4.896711	0.789106
H	11.933742	5.707736	2.166226
H	13.842105	-0.149614	-0.105179
H	12.147826	-0.038651	0.398365
H	13.376710	-0.713780	1.488907
H	18.696736	1.800480	0.643160
O	19.091153	2.618750	1.011101
H	19.516577	3.053242	0.266632
H	16.876740	0.465564	0.647464
O	17.674044	0.406197	0.078296
H	17.995521	-0.494795	0.177279

Model D

43

scf done: -940.624219

O	15.903728	1.102981	1.793657
O	17.359271	1.661106	3.805113
N	16.921475	2.914034	4.256215
C	14.873904	1.989802	1.882799
C	15.016827	3.219153	2.548315
C	13.908278	4.074081	2.633143
C	12.680955	3.754205	2.061799
C	12.581451	2.530600	1.388388
C	13.647615	1.641171	1.286660
C	16.344250	3.701592	3.074460
C	18.107925	3.659558	4.802040
C	15.905993	2.717303	5.339985
C	11.499432	4.691014	2.146898
C	13.511880	0.325414	0.565172
H	16.542065	1.261317	2.574091

H	14.022206	5.025070	3.146171
H	11.634711	2.254753	0.931945
H	16.246561	4.733713	3.414333
H	17.137173	3.650195	2.325456
H	18.804820	3.825066	3.983163
H	18.557249	3.028813	5.566327
H	17.771669	4.605341	5.229515
H	15.083183	2.138465	4.930047
H	16.388556	2.170846	6.147130
H	15.550355	3.690743	5.681642
H	10.622101	4.190236	2.567450
H	11.215762	5.065661	1.158067
H	11.722717	5.555303	2.776138
H	14.158070	0.287052	-0.317334
H	12.482692	0.167386	0.238002
H	13.804332	-0.508181	1.209808
H	18.925702	2.122090	2.514511
O	19.388024	2.804462	2.004637
H	19.595726	2.396869	1.143758
H	17.984833	0.742456	5.247676
O	18.220327	0.546295	6.179069
H	18.838011	-0.189245	6.154795
H	19.810830	1.973367	-1.322295
O	19.676492	1.483694	-0.506072
H	18.814589	1.028568	-0.603098
H	16.702010	0.531994	0.269554
O	17.194580	0.236420	-0.523380
H	17.173424	-0.724893	-0.500807

Sets of coordinates obtained at the ωB97XD/6-311++G(d,p) level of theory

Compound 1

Model A - monohydrated form

34

scf done: -710.974108

O	16.416340	1.561935	1.409566
O	17.715482	1.950463	3.616781
N	17.069178	3.015260	4.208963
C	15.292941	2.270252	1.604643
C	15.232650	3.369349	2.471982
C	14.014840	4.034436	2.648516
C	12.866557	3.657787	1.971611
C	12.964790	2.579055	1.087851
C	14.145363	1.881201	0.890293
C	16.458792	3.914402	3.146616
C	18.069203	3.804716	4.982313
C	16.028467	2.486721	5.127535
C	11.557782	4.378683	2.166893
C	14.237141	0.716708	-0.054166
H	16.996978	1.648568	2.217993
H	13.977332	4.885476	3.324642
H	12.079960	2.267568	0.537992
H	16.216129	4.861169	3.633916
H	17.279690	4.078771	2.445003
H	18.780363	4.233320	4.278120
H	18.581824	3.109269	5.643471
H	17.564388	4.586012	5.553239
H	15.353974	1.864258	4.545723
H	16.537246	1.887577	5.879461
H	15.481008	3.313132	5.585403
H	10.806645	3.720972	2.614817
H	11.155659	4.734327	1.214096
H	11.676807	5.244128	2.822565
H	14.960959	0.913977	-0.849498
H	13.267977	0.505256	-0.509926

H	14.585068	-0.178312	0.468048
O	19.741548	3.300763	2.338933
H	19.136684	2.645509	2.740748
H	19.964237	2.957591	1.473957

Model B

37

scf done: -787.424895

O	16.404105	1.570174	1.331179
O	17.663550	1.859133	3.597610
N	17.045210	2.935513	4.214136
C	15.281429	2.277720	1.554432
C	15.229736	3.341412	2.464013
C	14.016166	4.007505	2.665453
C	12.866656	3.665227	1.972607
C	12.958350	2.621731	1.047106
C	14.134516	1.923773	0.823288
C	16.459426	3.854201	3.157435
C	18.070790	3.691119	4.992679
C	15.989093	2.426603	5.131326
C	11.562630	4.387465	2.192063
C	14.217961	0.796625	-0.166377
H	16.967253	1.609223	2.147000
H	13.983982	4.831530	3.374186
H	12.072695	2.338448	0.483668
H	16.228406	4.795375	3.660121
H	17.287546	4.020129	2.465079
H	18.798012	4.091398	4.288045
H	18.547477	2.984457	5.669902
H	17.583531	4.494205	5.547704
H	15.303502	1.820816	4.544538
H	16.476989	1.820156	5.892181
H	15.460282	3.271485	5.576136
H	10.790866	3.706596	2.563261
H	11.191882	4.826320	1.261302

H	11.673715	5.194095	2.919965
H	14.948711	1.016890	-0.949197
H	13.248762	0.617270	-0.635440
H	14.550029	-0.123681	0.320993
H	19.087372	2.543433	2.659987
O	19.691360	3.176114	2.229538
H	19.764860	2.885062	1.320581
H	18.301382	0.812344	4.925389
O	18.505239	0.535017	5.839563
H	19.139553	-0.177661	5.774052

Model C

37

scf done: -787.417341

O	16.580729	1.744942	1.071822
O	17.368202	1.584912	3.499570
N	17.057584	2.780355	4.107502
C	15.381019	2.303386	1.364325
C	15.257372	3.244306	2.391038
C	13.999212	3.767733	2.690931
C	12.867670	3.384720	1.986039
C	13.030128	2.466833	0.945763
C	14.262224	1.918048	0.614215
C	16.479828	3.750176	3.095823
C	18.313051	3.354318	4.659525
C	16.087299	2.539301	5.212270
C	11.504522	3.930229	2.323455
C	14.425590	0.933399	-0.509273
H	17.075224	1.647003	1.940037
H	13.909861	4.500668	3.488814
H	12.158270	2.162957	0.372171
H	16.264287	4.681064	3.624895
H	17.289162	3.926189	2.383996
H	19.005782	3.488733	3.831473
H	18.720613	2.628322	5.359335

H	18.108716	4.304553	5.156799
H	15.188615	2.098044	4.787476
H	16.548629	1.827840	5.893958
H	15.866421	3.480794	5.718751
H	10.865788	3.152202	2.752204
H	11.000965	4.315096	1.432749
H	11.571046	4.743582	3.049151
H	15.064456	1.346312	-1.295267
H	13.458404	0.677066	-0.944983
H	14.906402	0.016896	-0.156556
H	17.330080	2.060069	-0.608666
O	17.620139	2.270750	-1.508086
H	18.064163	1.480666	-1.815250
H	14.590217	0.163893	2.865777
O	15.055633	-0.091358	3.664493
H	15.922963	0.341081	3.587621

Model D

43

scf done: -940.321227

O	16.172074	1.350472	1.551886
O	17.413468	1.719601	3.728504
N	16.968753	2.936857	4.223313
C	15.083857	2.149023	1.703917
C	15.147884	3.309096	2.481147
C	13.997458	4.088172	2.626190
C	12.804714	3.754881	2.002117
C	12.786599	2.605167	1.209786
C	13.899992	1.792890	1.046205
C	16.441024	3.784931	3.083262
C	18.124166	3.645222	4.850821
C	15.913803	2.686512	5.243352
C	11.567405	4.600287	2.157379
C	13.864414	0.553079	0.197900
H	16.734501	1.428945	2.392300

H	14.048776	4.990479	3.230033
H	11.865360	2.328739	0.703536
H	16.311595	4.793425	3.480123
H	17.261004	3.794766	2.360968
H	18.852596	3.852166	4.068176
H	18.542078	2.975083	5.600001
H	17.770599	4.568962	5.311445
H	15.123565	2.108737	4.770769
H	16.366859	2.119021	6.054084
H	15.523578	3.641281	5.600290
H	10.754663	4.029134	2.615267
H	11.210896	4.958561	1.187642
H	11.758722	5.472381	2.785957
H	14.605276	0.595951	-0.604922
H	12.879538	0.418461	-0.251962
H	14.094144	-0.334967	0.793787
H	18.998789	2.193394	2.592408
O	19.515658	2.822158	2.071262
H	19.352587	2.560721	1.151758
H	17.993343	0.759049	5.150614
O	18.190644	0.552055	6.083717
H	18.896163	-0.093756	6.076125
H	17.485419	2.038354	0.061003
O	18.340635	1.936853	-0.371264
H	18.357340	0.989083	-0.555350
H	16.682685	-0.189535	0.535188
O	17.193110	-0.695873	-0.113459
H	17.436017	-1.513950	0.319666

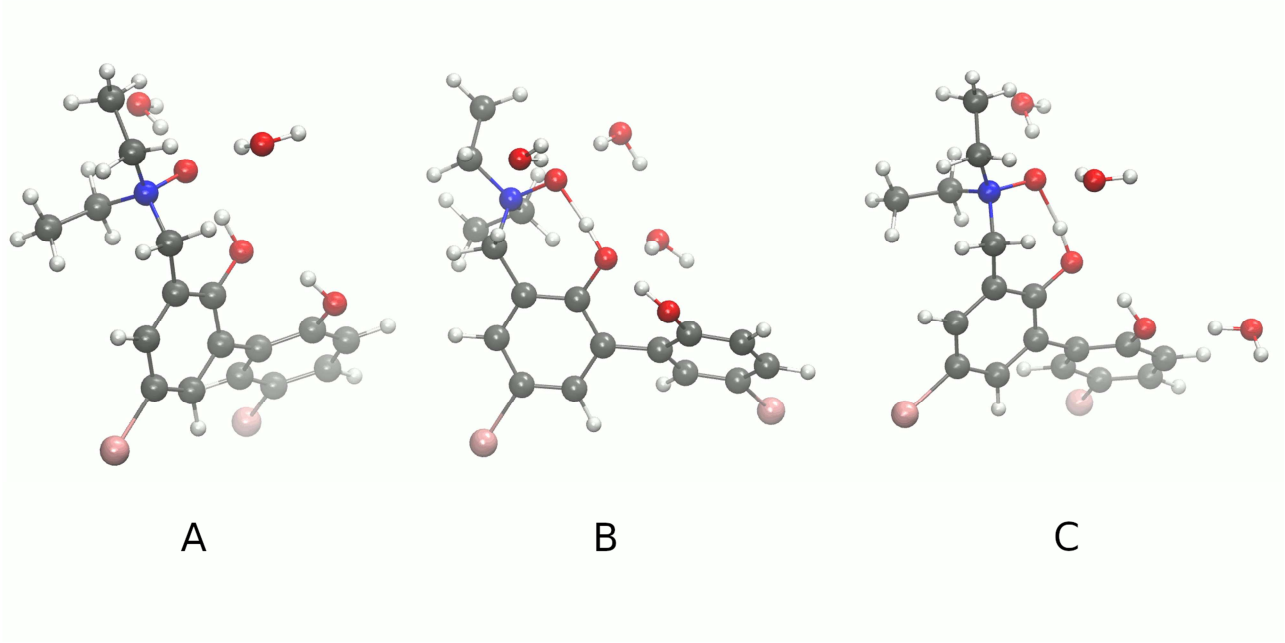

Figure S4. Microsolvation models of the compound **2** obtained at the ωB97XD/6-311++G(d,p) level of theory.

Table S6. Metric parameters of the intra- and intermolecular hydrogen bonds obtained as a result of microsolvation of the compound **2** (B3LYP/6-311++G(d,p) level of theory).. The interatomic distances are given in Å while valence angle is given in [°].

Compound 2								
	B3LYP/6-311++G(d,p)							
	Model A							
	Intramolecular hydrogen bond (interatomic distances)							
	O2...O1	O2-HBP1	HBP1...O2	<O2HBP1O1	O3...O2	O3-HBP2	HBP2...O2	<O3HBP2O2
	2.5266	1.0231	1.5089	172.34	2.6616	0.9752	1.7595	152.24
	Intermolecular hydrogen bonds (interatomic distances)							
	O1...O	O-H	O1...H	<O1HO	---	---	---	---
H_2O (1)	2.8106	0.9767	1.8511	166.70	---	---	---	---
H_2O (2)	2.8175	0.9758	1.9020	155.17	---	---	---	---
	Model B							
	Intramolecular hydrogen bond (interatomic distances)							
	O2…O1	O2-HBP1	HBP1…O2	<O2HBP1O1	O3…O2	O3-HBP2	HBP2…O2	<O3HBP2O2
	2.4757	1.0516	1.4273	174.08	2.6820	0.9745	1.7893	150.72
	Intermolecular hydrogen bonds (interatomic distances)							
	O1...O	O-H	O1...H	<O1HO	O2...O	O-H	O2...H	<O2HO
H_2O (1)	2.8071	0.9757	1.8972	154.04	2.9532	0.9696	2.0396	156.28
H_2O (2)	2.9302	0.9693	1.9894	163.02	---	---	---	---

Table S6 (Continuation). Metric parameters of the intra- and intermolecular hydrogen bonds obtained as a result of microsolvation of the compound **2** (B3LYP/6-311++G(d,p) level of theory). The interatomic distances are given in Å while valence angle is given in [°].

Compound 2								
	B3LYP/6-311++G(d,p)							
	Intramolecular hydrogen bond (interatomic distances)							
	O2...O1	O2-HBP1	HBP1...O2	<O2HBP1O1	O3...O2	O3-HBP2	HBP2...O2	<O3HBP2O2
	2.5147	1.0278	1.4919	172.66	2.6272	0.9796	1.7183	152.63
	Intermolecular hydrogen bonds (interatomic distances)							
	O1...O	O-H	O1...H	<O1HO	O3...O	O-H	O3...H	<O3HO
H_2O (1)	2.8151	0.9762	1.8588	165.71	2.8813	0.9707	1.9182	171.21
H_2O (2)	2.8215	0.9752	1.9118	154.12	---	---	---	---

Table S7. Metric parameters of the intra- and intermolecular hydrogen bonds obtained as a result of microsolvation of the compound **2** (ωB97XD/6-311++G(d,p) level of theory). The interatomic distances are given in Å while valence angle is given in [°].

Compound 2								
	ωB97XD/6-311++G(d,p)							
	Model A							
	Intramolecular hydrogen bond (interatomic distances)							
	O2...O1	O2-HBP1	HBP1...O2	<O2HBP1O1	O3...O2	O3-HBP2	HBP2...O2	<O3HBP2O2
	2.5276	1.0122	1.5227	171.10	2.6666	0.9702	1.7750	151.22
	Intermolecular hydrogen bonds (interatomic distances)							
	O1...O	O-H	O1...H	<O1HO	---	---	---	---
H_2O (1)	2.7723	0.9727	1.8613	154.72	---	---	---	---
H_2O (2)	2.7745	0.9737	1.8193	166.16	---	---	---	---
	Model B							
	Intramolecular hydrogen bond (interatomic distances)							
	O2...O1	O2-HBP1	HBP1...O2	<O2HBP1O1	O3...O2	O3-HBP2	HBP2...O2	<O3HBP2O2
	2.4686	1.0393	1.4350	172.15	2.6833	0.9696	1.8068	148.76
	Intermolecular hydrogen bonds (interatomic distances)							
	O1...O	O-H	O1...H	<O1HO	O2...O	O-H	O2...H	<O2HO
H_2O (1)	2.7619	0.9730	1.8548	153.89	2.8799	0.9661	1.9907	152.04
H_2O (2)	2.8809	0.9666	1.9434	162.78	---	---	---	---

Table S7 (Continuation). Metric parameters of the intra- and intermolecular hydrogen bonds obtained as a result of microsolvation of the compound **2** (ωB97XD/6-311++G(d,p) level of theory). The interatomic distances are given in Å while valence angle is given in [°].

Compound 2								
	ωB97XD/6-311++G(d,p)							
	Model C							
	Intramolecular hydrogen bond (interatomic distances)							
	O2...O1	O2-HBP1	HBP1...O2	<O2HBP1O1	O3...O2	O3-HBP2	HBP2...O2	<O3HBP2O2
	2.5170	1.0159	1.5080	171.39	2.6285	0.9743	1.7307	151.52
	Intermolecular hydrogen bonds (interatomic distances)							
	O1...O	O-H	O1...H	<O1HO	O3...O2	O3-HBP2	HBP2...O2	<O3HBP2O2
H_2O (1)	2.7750	0.9724	1.8693	153.77	2.8524	0.9670	1.8983	168.45
H_2O (2)	2.7768	0.9733	1.8237	165.54				

MICROSOLVATION MODELS OF THE COMPOUND 2

Sets of coordinates obtained at the B3LYP/6-311++G(d,p) level of theory

Compound 2

Model A

48

scf done: -6241.115307

Br	3.957661	2.217929	-4.649697
Br	6.575341	7.256155	0.406954
O	9.112137	1.189110	-1.625247
O	10.263554	3.428306	-2.488018
O	12.322647	4.746570	-3.125037
C	7.466582	2.808989	-2.420823
C	7.971200	1.495071	-2.297952
C	7.253591	0.420986	-2.834423
H	7.661297	-0.574219	-2.704912
C	6.060367	0.614491	-3.515208
H	5.520126	-0.227598	-3.927941
C	5.583290	1.912460	-3.672363
C	6.269251	2.990319	-3.136509
H	5.883344	3.991905	-3.275089
C	8.078230	4.003432	-1.771949
C	9.457513	4.296698	-1.836081
C	9.978061	5.459064	-1.229771
C	9.106893	6.337705	-0.578628
H	9.495663	7.225113	-0.094347
C	7.750955	6.053383	-0.515387
C	7.241279	4.899777	-1.093368
H	6.185725	4.677249	-1.011144
C	11.461222	5.729456	-1.135062
H	11.996370	4.886877	-0.693355
H	11.626219	6.607972	-0.512046
N	12.207437	5.972437	-2.453478
C	13.606248	6.464775	-2.098107
H	13.478452	7.384450	-1.524586

H	14.012495	5.696929	-1.441053
C	14.511720	6.677185	-3.298808
H	15.512754	6.906209	-2.924902
H	14.194490	7.509834	-3.929052
H	14.575361	5.781474	-3.914542
C	11.471254	6.932467	-3.371851
H	10.493764	6.478078	-3.524604
H	12.005268	6.886501	-4.318518
C	11.340444	8.361705	-2.862924
H	10.748218	8.920670	-3.591523
H	12.303872	8.866692	-2.773347
H	10.817261	8.426093	-1.907529
H	9.771019	1.887752	-1.795125
H	11.131454	3.891672	-2.768706
H	13.484195	3.620294	-2.125051
O	13.997355	3.351081	-1.340020
H	14.190657	2.415208	-1.443507
H	12.627428	4.831560	-4.948897
O	12.835776	5.093080	-5.866576
H	12.431834	4.427564	-6.430284

Model B

51

scf done: -6317.585502

Br	-5.520416	-0.854302	-1.143819
Br	-0.291065	4.585950	0.036164
O	-0.932308	-1.687540	2.732546
O	0.909335	-1.297978	0.822178
O	3.252512	-1.739183	0.155948
C	-1.821653	-0.477771	0.806302
C	-1.915166	-1.455067	1.822613
C	-3.089486	-2.202109	1.964504
H	-3.133252	-2.928747	2.766702
C	-4.167435	-2.024600	1.109254
H	-5.067888	-2.612535	1.231282

C	-4.061784	-1.089825	0.082738
C	-2.913602	-0.328747	-0.068222
H	-2.848878	0.389547	-0.875221
C	-0.671745	0.459191	0.658187
C	0.671859	0.029067	0.664530
C	1.726165	0.951371	0.500220
C	1.420863	2.301078	0.299666
H	2.220152	3.022319	0.180419
C	0.100438	2.726141	0.287894
C	-0.935260	1.822770	0.473758
H	-1.959549	2.170715	0.490894
C	3.185664	0.584473	0.656538
H	3.396800	0.190037	1.652325
H	3.792950	1.476315	0.504615
N	3.735833	-0.495750	-0.279238
C	5.251894	-0.502568	-0.130235
H	5.602550	0.486240	-0.430038
H	5.426140	-0.628126	0.937824
C	5.939538	-1.603934	-0.918381
H	7.000265	-1.592290	-0.656076
H	5.862933	-1.466582	-1.998228
H	5.536801	-2.582252	-0.659908
C	3.295018	-0.303457	-1.721703
H	2.207118	-0.309427	-1.689920
H	3.602323	-1.210744	-2.237273
C	3.817035	0.953320	-2.403703
H	3.380393	0.991371	-3.404568
H	4.901900	0.949426	-2.524239
H	3.520901	1.869385	-1.889221
H	-0.068723	-1.603553	2.289025
H	1.904745	-1.533914	0.578597
H	3.972899	-2.107793	1.871860
O	4.426065	-1.870055	2.702633
H	4.296056	-2.604219	3.309341
H	3.070457	-3.162815	-1.221731

O	2.848432	-3.645110	-2.032724
H	1.884177	-3.558433	-2.079589
H	0.099988	-2.396292	-0.693980
O	0.056438	-2.792457	-1.577901
H	-0.828118	-3.162493	-1.655500

Model C

51

scf done: -6317.582662

Br	-5.458306	-0.189571	-1.728928
Br	-0.088311	4.504577	0.954862
O	-1.070537	-2.221494	1.934455
O	0.864817	-1.440385	0.338757
O	3.192684	-1.717432	-0.571155
C	-1.844165	-0.511869	0.378899
C	-2.019644	-1.721311	1.082824
C	-3.214532	-2.435983	0.974647
H	-3.317332	-3.354704	1.540330
C	-4.245597	-1.986970	0.160479
H	-5.165792	-2.550867	0.080862
C	-4.065326	-0.812060	-0.562809
C	-2.889615	-0.085629	-0.459597
H	-2.767065	0.819813	-1.039451
C	-0.653099	0.372728	0.521097
C	0.673013	-0.108678	0.478741
C	1.766677	0.775188	0.586687
C	1.525131	2.146312	0.713015
H	2.355187	2.834839	0.813381
C	0.223036	2.623166	0.752511
C	-0.853329	1.752051	0.668017
H	-1.862989	2.136091	0.728307
C	3.191678	0.288973	0.711903
H	3.299634	-0.431678	1.524632
H	3.843605	1.138090	0.914467
N	3.782412	-0.446652	-0.497626

C	5.274949	-0.620303	-0.237094
H	5.691033	0.381828	-0.119972
H	5.330893	-1.136236	0.720602
C	6.004687	-1.404992	-1.313342
H	7.027087	-1.574436	-0.966470
H	6.061202	-0.872067	-2.264067
H	5.539192	-2.373816	-1.486977
C	3.501408	0.267409	-1.808553
H	2.416414	0.343246	-1.857983
H	3.816360	-0.427085	-2.584382
C	4.156774	1.632549	-1.968432
H	3.828262	2.048547	-2.923950
H	5.246314	1.575759	-1.997834
H	3.860459	2.339730	-1.192014
H	-0.190706	-2.108096	1.518836
H	1.808002	-1.630496	-0.022748
H	3.755492	-2.733312	0.947443
O	4.148682	-2.842692	1.833115
H	3.880626	-3.709977	2.149698
H	3.261443	-2.565285	-2.223846
O	3.458484	-2.835418	-3.140985
H	2.739796	-3.415028	-3.408242
H	-1.417267	-3.796625	2.972837
O	-1.699186	-4.622307	3.398357
H	-1.736961	-4.422528	4.337881

Sets of coordinates obtained at the ωB97XD/6-311++G(d,p) level of theory

Compound 2

Model A

48

scf done: -6240.826831

Br	4.093683	2.276854	-4.771849
Br	6.640192	7.296014	0.338113
O	9.069263	1.206017	-1.532115
O	10.283171	3.396084	-2.448922
O	12.324117	4.726674	-3.121703
C	7.497425	2.828417	-2.423434
C	7.968065	1.514423	-2.254650
C	7.254356	0.448743	-2.802033
H	7.634138	-0.552579	-2.639370
C	6.099410	0.656759	-3.534869
H	5.558976	-0.181469	-3.956372
C	5.656108	1.957308	-3.735067
C	6.342136	3.026232	-3.188604
H	5.985287	4.035450	-3.355855
C	8.111718	4.016591	-1.771256
C	9.489691	4.282366	-1.819755
C	10.017845	5.435590	-1.216695
C	9.156144	6.330828	-0.588366
H	9.554053	7.217615	-0.108374
C	7.797347	6.073875	-0.541562
C	7.280177	4.925455	-1.116647
H	6.218799	4.719306	-1.053094
C	11.499791	5.690752	-1.133055
H	12.033442	4.839830	-0.703746
H	11.679393	6.563251	-0.504756
N	12.206634	5.937068	-2.454111
C	13.591074	6.451513	-2.133825
H	13.463235	7.370259	-1.558203
H	14.030244	5.693470	-1.485151
C	14.452271	6.678130	-3.357825

H	15.458727	6.930730	-3.017805
H	14.092923	7.499998	-3.979832
H	14.512338	5.780544	-3.971589
C	11.439510	6.877948	-3.345584
H	10.466066	6.408002	-3.480387
H	11.951002	6.850308	-4.306182
C	11.300048	8.293962	-2.818816
H	10.662316	8.846999	-3.511053
H	12.257751	8.815574	-2.769225
H	10.822207	8.333634	-1.838404
H	9.749867	1.875568	-1.704525
H	11.139450	3.847234	-2.745147
H	13.445832	3.639125	-2.110145
O	13.928502	3.378855	-1.306563
H	14.090279	2.438206	-1.373556
H	12.599639	4.860941	-4.915014
O	12.780549	5.159358	-5.824007
H	12.342082	4.533096	-6.399405

Model B

51

scf done: -6317.277158

Br	-5.320206	-0.870223	-1.238296
Br	-0.094978	4.579656	-0.015538
O	-1.013985	-1.491611	2.941602
O	0.882026	-1.264931	1.056506
O	3.116070	-1.853631	0.186834
C	-1.788152	-0.381295	0.927194
C	-1.938531	-1.309228	1.972137
C	-3.111059	-2.059145	2.066832
H	-3.203409	-2.754500	2.892189
C	-4.125088	-1.928770	1.134835
H	-5.026451	-2.522655	1.219476
C	-3.960973	-1.038775	0.080584
C	-2.812577	-0.274790	-0.021682
H	-2.693889	0.413614	-0.850086

C	-0.618972	0.528024	0.787662
C	0.699855	0.050813	0.815391
C	1.778318	0.912906	0.567366
C	1.523218	2.257280	0.310333
H	2.348142	2.935789	0.124683
C	0.224821	2.737424	0.312106
C	-0.838957	1.883345	0.547012
H	-1.853052	2.263840	0.546803
C	3.215860	0.462052	0.623283
H	3.485698	0.072303	1.607318
H	3.863675	1.309555	0.398854
N	3.591405	-0.656140	-0.331712
C	5.098845	-0.732197	-0.375035
H	5.458823	0.235117	-0.730049
H	5.404033	-0.859248	0.663968
C	5.613805	-1.868664	-1.232817
H	6.693361	-1.941872	-1.087243
H	5.429218	-1.709421	-2.296658
H	5.162262	-2.814575	-0.935781
C	2.989807	-0.472944	-1.702483
H	1.911102	-0.460956	-1.550764
H	3.216842	-1.389655	-2.243367
C	3.460555	0.762977	-2.444525
H	2.907653	0.816353	-3.384192
H	4.523111	0.722219	-2.692758
H	3.256779	1.685409	-1.897255
H	-0.132509	-1.452096	2.539768
H	1.826404	-1.570902	0.748931
H	3.979950	-2.163158	1.798724
O	4.511190	-1.899337	2.569983
H	4.426435	-2.598305	3.217814
H	2.701357	-3.220275	-1.131093
O	2.389401	-3.670367	-1.927589
H	1.464916	-3.398423	-1.981624
H	-0.040909	-2.106787	-0.493453

O	-0.146096	-2.265515	-1.440608
H	-1.091438	-2.339502	-1.581023

Model C

51

scf done: -6317.270108

Br	-5.371614	-0.119916	-1.786743
Br	0.066570	4.475800	0.929887
O	-1.140313	-2.129430	2.018470
O	0.817851	-1.473272	0.392483
O	3.120703	-1.792734	-0.572003
C	-1.839331	-0.465889	0.401014
C	-2.058197	-1.640743	1.136811
C	-3.263623	-2.328472	1.023283
H	-3.403030	-3.226693	1.614571
C	-4.258726	-1.879663	0.171637
H	-5.191283	-2.423068	0.087281
C	-4.034862	-0.736097	-0.582943
C	-2.845313	-0.039028	-0.473114
H	-2.683269	0.846828	-1.075273
C	-0.627403	0.385098	0.545083
C	0.674231	-0.140434	0.516355
C	1.790308	0.704642	0.625665
C	1.594835	2.078714	0.735323
H	2.448350	2.739989	0.832096
C	0.313371	2.600997	0.758872
C	-0.786971	1.764752	0.675696
H	-1.786447	2.179589	0.721002
C	3.193673	0.168828	0.737109
H	3.280522	-0.571363	1.535779
H	3.876257	0.990925	0.952474
N	3.729864	-0.548927	-0.488498
C	5.213136	-0.749121	-0.278590
H	5.652427	0.242266	-0.152103
H	5.293097	-1.287972	0.665700

C	5.886548	-1.516109	-1.396381
H	6.918467	-1.709403	-1.096083
H	5.909924	-0.959351	-2.334976
H	5.395522	-2.471809	-1.573859
C	3.427342	0.194795	-1.762850
H	2.342221	0.288368	-1.783773
H	3.711942	-0.479748	-2.568508
C	4.100123	1.548461	-1.892359
H	3.739256	2.014852	-2.811025
H	5.185857	1.467659	-1.971798
H	3.852788	2.221949	-1.069905
H	-0.258825	-2.073560	1.607293
H	1.735211	-1.691850	0.014793
H	3.654636	-2.779328	0.923267
O	4.029129	-2.877330	1.815246
H	3.734094	-3.724590	2.148177
H	3.167993	-2.563920	-2.223943
O	3.350646	-2.793493	-3.151978
H	2.600306	-3.306725	-3.450537
H	-1.619599	-3.665321	3.025938
O	-2.019796	-4.451128	3.422815
H	-2.129540	-4.236479	4.348925

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[2] Wojciechowski, G.; Ratajczak-Sitarz, M.; Katrusiak, A.; Brzeziński, B. *J. Mol. Struct.* **2002**, *612*, 59-64.